

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01F 1/00, 1/44, B01J 27/20, 35/06	A2	(11) International Publication Number: WO 99/46782 (43) International Publication Date: 16 September 1999 (16.09.99)
(21) International Application Number: PCT/NL99/00116 (22) International Filing Date: 4 March 1999 (04.03.99) (30) Priority Data: 1008528 9 March 1998 (09.03.98) NL (71) Applicants (for all designated States except US): UNIVER- SITEIT UTRECHT [NL/NL]; Heidelberglaan 8, NL-3584 CS Utrecht (NL). U-CAT B.V. [NL/NL]; Bernadottelaan 15, NL-3527 GA Utrecht (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): GEUS, John, Wilhelm [NL/NL]; Gezichtslaan 100, NL-3723 GJ Bilthoven (NL). (74) Agent: OTTEVANGERS, S., U.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW); Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM); European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE); OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>In English translation (filed in Dutch). Without international search report and to be republished upon receipt of that report.</i>
(54) Title: FERROMAGNETIC PARTICLES (57) Abstract The present invention relates to ferromagnetic metal particles comprising a core of a ferromagnetic metal or metal alloy, wherein the surface of the core is covered entirely with a layer of graphitic carbon.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Title: Ferromagnetic particles

The invention relates to chemically inert ferromagnetic particles having dimensions of about 4 nm to 1 μm , which can be dispersed in liquids. The invention also relates to the preparation of such particles. The

5 ferromagnetic particles can be utilized in so-called ferrofluids, where, through dispersion of small magnetic particles in liquids, magnetic forces can be exerted on these liquids. These ferromagnetic particles can also be used for biophysical or biomedical applications. Also considered, in

10 particular, are analytic methodologies whereby certain biologically important molecules, macromolecules or cells can be separated. Proteins or, by means of proteins, cells, can be adhered to the ferromagnetic particles, and the proteins or cells can be separated with magnetic forces. To remove

15 toxic metals or radioactive components occurring in low concentrations from liquid flows, adsorption onto magnetic particles has also been proposed (L. Nuñez and M.D. Kaminski, ChemTech September 1998, pp. 41-46). It has further been proposed to apply magnetic particles in NMR imaging

20 techniques. In addition, the use of ferromagnetic particles for reprographic purposes has been proposed. It is also possible to selectively heat material adhered to the magnetic particles by exposing the material adhered to the magnetic particles to a suitable electric alternating field. A special

25 application of magnetic particles according to the invention is as support for catalytically active materials or enzymes. These catalytically active materials include *inter alia* catalytically active noble metals, such as platinum, palladium and rhodium, catalytically active metals, such as

30 nickel, copper or iron, catalytically active oxides, such as manganese oxide and copper oxide, and catalytically active sulfides, such as cobalt sulfide. Also homogeneous catalysts can be adhered to the ferromagnetic particles and in this way, after completion of the reaction, be readily separated

35 from the reaction products. In particular, it is attractive

to separate organometallic compounds with costly metals, used as homogeneous catalysts, and ligands, from liquids through adherence to ferromagnetic particles.

In the use of catalysts in chemical reactions that
5 proceed in a liquid phase, generally no catalyst bodies of too small a size can be used. If a fixed catalyst bed is used through which a liquid flow is passed, the pressure drop becomes too high in the case of particles smaller than about 0.1 mm. At a technically useful linear velocity of the
10 liquid, the catalyst is pushed out of the reactor or the pressure drop becomes unacceptably high. If the catalyst is suspended in the liquid, smaller catalyst bodies can be used. Following the reaction, the catalyst bodies must be separated from the liquid by filtration or centrifugation. Such a
15 separation is possible only with catalyst bodies of dimensions of at least about 3 mm. According to the current state of the art, smaller catalyst bodies cannot be properly separated from the liquid. Because the presence of catalyst residues in the reaction products is mostly not allowable,
20 often costly procedures are necessary to remove the catalyst residues from the reaction products. As a consequence, stringent requirements are imposed on the wear resistance of catalyst bodies that are used while suspended in liquids. Upon wear of catalyst bodies, particles smaller than about 1
25 mm are formed, which cannot be separated from the liquid anymore by the conventional methods.

The active surface area per unit weight of the catalyst determines the activity. In general, the surface area per unit weight of the catalyst in particles of at least
30 3 mm is too small to obtain the technically required activity. In general, therefore, porous catalyst bodies are used. The internal surface of the catalyst bodies having minimal dimensions of about 3 μm is sufficiently large to obtain technically required activities. It is technically not
35 easy to produce wear-resistant catalyst bodies of dimensions of, for instance, 3 to 10 μm on a large scale. Comparatively

new is the production of such catalyst bodies by spray-drying. With this technique it is possible to manufacture porous bodies based on aluminum oxide or silicon oxide having dimensions of, for instance, from 3 to 10 μm . However,
5 manufacturing porous bodies based on activated carbon, which is a widely used support for liquid phase reaction, is not possible in this way.

With porous bodies having dimensions of from 10 to 100 μm , in reactions in the liquid phase, trouble may be
10 caused by transport impediments due to the pores in the catalyst bodies. First of all, this may lead to a reduction of the activity. Much more serious in general, however, is the effect of transport impediments on the selectivity of the catalytic reaction. A lower selectivity of a catalytic
15 reaction can lead to products for which it is difficult to find a destination, while the consumption of raw materials increases. Often, an unwanted reaction may also lead to molecules which block the pores of the catalyst bodies. In that case, the activity of the catalyst decreases. If
20 regeneration of the catalyst is possible at all, the catalyst must be separated from the liquid and treated at elevated temperature in a gas flow.

If ferromagnetic particles are used as catalytically active material or as support for catalytically active
25 material, separation of the catalyst bodies is technically properly possible also in the case of particles of considerably smaller dimensions than about 3 μm . By applying an inhomogeneous magnetic field, extremely small particles too can be readily separated from liquids. Very small
30 particles can be employed then and transport impediments can thus be avoided. Technically, this is of great importance; avoiding transport impediments can lead to particularly attractive selectivities in liquid phase reactions.

In many cases, catalytic reactions are carried out in
35 which at least one of the reactants is liquid and at least one of the other reactants is gaseous. The transport of the

gaseous reactant to the catalyst surface can in many cases be rate-determining, especially when the solubility of the gas in the liquid is low. For instance, in carrying out hydrogenation reactions, a deficiency of hydrogen on the catalyst surface can lead to unwanted reactions of partially hydrogenated intermediates. Now, if the catalyst bodies are made significantly smaller than the thickness of the laminar boundary layer around the gas bubbles which are passed through the liquid, a much faster transport of the gaseous reactant to the catalyst surface can be accomplished. The thickness of the laminar boundary layer can be set at about 10 μm , so that catalyst particles of dimensions less than 1 μm lead to a faster mass transfer from the gas bubbles to the catalyst surface. Naturally, the presence of such small catalyst bodies is effective only if the catalyst bodies are not present in the liquid while agglomerated to clusters of particles.

A last important application of ferromagnetic particles according to the invention is as electrodes for electrochemical reactions. A great drawback of state of the art electrodes is that either the surface accessible to reactants is small or the electric conductance of the electrode is low. Because a low electric conductance is highly objectionable, electrodes having relatively low surface areas are employed. For the application of electrochemical processes, this has always been a major drawback; electrochemical processes nearly always have a low production rate per unit volume, so that such processes are relatively costly. With ferromagnetic particles having a high intrinsic electric conductance, electrodes can be achieved in which a high surface area is combined with a high electric conductance.

According to the prior art, small ferromagnetic particles are already being used. Most well-known is the application in the above-mentioned ferrofluids (a review of the older literature is given in B. Berkovsky,

Thermomechanics of Magnetic Fluids, Hemisphere Publishing Corporation, Washington 1978; a more recent review is given in La Recherche 18 (192) October 1987, pp. 1150-1159).

- 5 Ferromagnetic particles of dimensions of less than 1 μm are prepared in many cases by grinding. However, this is a very costly method, since the material often needs to be ground for weeks on end. It will be clear that grinding can only be properly applied in the case of oxidic ferromagnetic materials; metals cannot be properly comminuted by grinding.
- 10 An alternative is precipitation of small ferromagnetic particles. In general, the precipitation is carried out according to a method dating from the last century, whereby solutions of iron(II) and iron(III) are mixed at a pH maintained constant. What precipitates then is, at least for
- 15 a part, magnetite, Fe_3O_4 , which can be converted by a thermal treatment to the more stable maghemite, $\gamma\text{-Fe}_2\text{O}_3$. A drawback of these ferromagnetic materials is the relatively high chemical reactivity; in many liquids, attack and dissolution of iron ions arises.
- 20 Another drawback is that the ferromagnetic particles have a poor dispersibility. Owing to the magnetic forces, there is an attractive interaction between the particles, which cluster as a result. In the ferrofluids, this drawback has been recognized. A stabilization of suspensions of
- 25 magnetic particles is accomplished in two ways. According to the first methodology, elongate molecules having a reactive group on one side are provided on the surface of the ferromagnetic particles. Detergents are a good example of such molecules. A polar head is adhered to the ferromagnetic
- 30 particle, while a non-polar tail projects into the liquid. The non-polar portions of the molecules prevent the distance between the ferromagnetic particles from becoming small and hence the attractive force between the particles from becoming large. Polymer molecules are also used for this
- 35 purpose. The second way of preventing clustering of ferromagnetic particles is to provide an electrostatic charge

on the particles. If, for instance, a negative charge is provided on the particles, this leads to electrostatic repulsion between the particles, which dominates over the magnetic attraction. However, this requires proper control of the ionic strength of the suspension, since too high an ionic strength leads to neutralization of the electrostatic charge on the particles over a short distance. Also, the electrostatic charge on suspended particles is generally strongly dependent on the pH of the suspension, so that the pH must be properly controlled as well.

The literature shows that the problems in the separation of suspended catalysts and enzymes from liquids have been recognized before. Thus, in EP-A 125 995 it is proposed to immobilize enzymes by binding the enzymes to ferromagnetic particles. In patent application WO 95/13874 (B.A.S.F.), it is proposed to use catalysts consisting of a ferromagnetic core, a binder and catalytically active compounds of metals. The binder is provided on ferromagnetic particles of a diameter of from 5 to 1000 nm and preferably from 5 to 100 nm. The saturation magnetization of the particles is from 20 to 200 nTm² per gram and preferably 30 to 100 nTm² per gram. The possibility of coprecipitating the catalytically active material with the ferromagnetic material is left open. Especially in the case of costly noble metals, however, this method is not attractive, because then a large fraction of the noble metal is not present on the surface of the ferromagnetic particles. It is therefore preferred to cover the ferromagnetic particles with one or more layers of a binder. Mentioned as binder are monomeric amines, such as pyridine or 4-pyridine-ethanesulfonic acid. Preferably used, however, are organic polymers which are soluble or dispersible in water. A series of such polymers are mentioned, such as polymers of acrylic acid, methacrylic acid and vinylsulfonic acid. Also mentioned are amides, such as vinyl pyrrolidone and acrylamide. The same application WO 95/13874 enumerates a long series of ferromagnetic materials

that are suitable for magnetic separation of material adhered thereto, such as magnetite, maghemite, chromium dioxide and manganese-zinc ferrite. Touched upon in addition is the possibility of using ferromagnetic metal particles, such as
5 iron, nickel or cobalt, obtained by decomposition of the corresponding carbonyls. It is rightly noted, however, that owing to the high saturation magnetization, these particles have a strong tendency to agglomerate.

Other patents also refer to covering ferromagnetic
10 particles with large non-magnetic molecules. Thus, EP 90420555 (Rhone-Poulenc Chimie) suggests covering ferromagnetic particles with polysilsesquioxane. U.S. 5,512,332 (Immunivest Corporation) mentions covering ferromagnetic particles with synthetic or naturally occurring
15 polymers, including peptides or proteins. The latter patent focuses especially on the separation of biologically or biochemically important species. The bioanalytic application comes first here. This last application also dominates in U.S. Patent 5,536,644 (Behringwerke AG, Marburg, Germany),
20 which focuses particularly on the separation of cells and microorganisms from aqueous liquids by binding them to ferromagnetic particles and separating the ferromagnetic particles in a magnetic field with a gradient.

In great detail, patent application WO 91/02811 of
25 Immunicon Corporation addresses the stability of suspensions of magnetic particles and the redispersion of such particles. In this patent application, the magnetic particles are preferably covered with a biochemical or biologically active material. After the discussion of the prior art, this patent
30 application describes the preparation of oxidic magnetic particles in the presence of a component suitable for forming a layer on the magnetic particles which counteracts conglomeration of the magnetic particles. Also described is a preparation whereby agglomerates of small magnetic particles
35 are broken up by contacting the suspension with compounds

suitable therefor. Such compounds are polypeptides, proteins or antibodies.

Finally, a publication of interest is one by M.J. Szymonifka and K.T Chapman in Tetrahedron Letters 36 (10) (1995) 1597-1600. These authors are concerned with synthesizing large numbers of different chemical compounds for the development of medicines. Porous beads of resin are prepared, in which the reagents needed are provided. For these beads to be handled by a robot, it has been found exceptionally suitable to include non-strongly permanently magnetized ferromagnetic particles in the beads. The beads can now be manipulated with magnets. The authors prepared magnetite particles in the presence of polydivinylbenzene. In this way, provided that the magnetite was prepared by iron(II) with aryl nitro groups, beads that could be magnetically manipulated were obtained.

The above review of the prior art shows that especially stabilization against agglomeration of ferromagnetic particles by providing non-magnetic layers on the ferromagnetic particles has been carried out. The provision of electrostatic charges on the ferromagnetic particles has received less attention. For all above-mentioned applications, however, the two above-mentioned methods of stabilizing suspensions of ferromagnetic particles are not attractive. If the dispersion of ferromagnetic particles is stabilized by an electrostatic charge, particular ions must be provided on the particles. The ions that are used to provide such a charge, such as anions of heteropolyacids, may have an undesirable catalytic effect or may react with catalytically active components to form inactive or little active compounds. In the other applications, the charge-determining ions will mostly interfere with the groups that are to bind the species to be separated. Stabilization by molecules having long non-polar groups has drawbacks in catalytic applications. Such a stabilization works only if the stabilizing molecules are

provided on the surface of the ferromagnetic particles in a relatively high density. Then it is only possible to provide the catalytically active components on the non-polar parts of the stabilizing molecules. Apart from possible transport
5 hindrance due to the typically closely packed non-polar molecules, the adherence of catalytically active components to such molecules is mostly low. Technically, loss of small catalytically active particles in the liquid phase is virtually never acceptable. In addition to the above-
10 mentioned contamination of the reaction products with the catalyst, this may lead to losses of costly catalytically active metals, such as rhodium.

The greatest drawback of the ferromagnetic particles proposed according to the prior art, however, is the chemical
15 reactivity of the ferromagnetic materials themselves. Magnetite and maghemite are attacked by water and react to form non-ferromagnetic hydrated iron oxides. In the presence of (weakly) acid aqueous solutions, the attack proceeds more rapidly. Chromium dioxide is not stable with respect to
20 disproportionation to chromic oxide and chromium trioxide (Cr_2O_3 and CrO_3). Chromium dioxide and the decomposition products are not resistant to acids and bases. The metals iron, nickel and cobalt, certainly when they are finely divided, are highly sensitive to oxidation to non-
25 ferromagnetic compounds. Coverage with a polymer layer will generally not protect the ferromagnetic particles against chemical interaction of the liquids in which the particles are used. It is not possible to provide a layer of molecules known according to the prior art which fully prevents contact
30 with the liquid.

A special method for the preparation of ferromagnetic particles is described in patent application WO95/01643 in the name of Carnegie Mellon University. In the preparation, use is made of a modification of the Kratschmer-Huffmann
35 carbon arc method. A hole is drilled in the carbon electrode and the thus obtained cavity is filled with a metal oxide

powder containing the components for the desired magnetic material. The metal oxide powder is fixed with graphite cement. Thereafter an arc is struck, whereby soot is formed. By magnetic route, more or fewer magnetic particles can now
5 be separated from the soot. As appears from an electron microscopic recording at high magnification, magnetic particles occur in the soot which are partly covered with layers having a graphite structure. Apart from the laborious preparation procedure, the ferromagnetic particles obtained
10 in this way are not completely surrounded by layers of carbon with a relatively inert graphite structure. As a consequence, aggressive molecules can relatively easily reach the surface of the magnetic phase and penetrate between the parts of the surface that are covered with layers of a graphite structure.

15 The object of the present invention, therefore, is to provide small ferromagnetic particles which are chemically inert. According to the invention, the desired particles are ferromagnetic metal particles which are completely covered with a layer of graphitic carbon. 'Graphitic' is described
20 herein as consisting of layers of carbon atoms having a graphite structure, while the successive layers are not stacked according to the graphite structure. It is surprising that it is possible to cover ferromagnetic metal particles so completely with a layer of carbon that the material exhibits
25 chemically a greater inertness than carbon which, for instance as activated carbon, is used as catalyst support. Like activated carbon, ferromagnetic particles provided with a layer of carbon can be affected only by strongly oxidizing agents.

30 Complete coverage of the ferromagnetic particles can be demonstrated experimentally in a number of different ways. The most obvious way is treatment of the carbon-encapsulated particles with a non-oxidizing (strongly) acid solution. For this purpose, for instance hydrochloric acid, formic acid or
35 acetic acid can be used. All metal particles that are not completely covered with carbon are thereby dissolved.

Examination in the electron microscope can also provide a definite answer regarding the extent to which the surface is covered with carbon. In general, the layer of carbon is properly recognizable in the microscope by a difference in contrast. At a high magnification, the carbon layers with a graphite structure, which have a mutual distance of about 0.35 nm, can be distinguished. Figure 1 shows a recording of an encapsulated metal particle at a relatively low magnification; it is clear that a carbon layer of a uniform thickness surrounds the particle completely. The structure of the carbon layer becomes clear from Figure 2, in which an electron microscope recording at a much higher magnification is shown. Now it is clear that the carbon layers have been deposited around the metal particle with a graphitic structure. The carbon layers follow the curve of the surface of the metal or alloy particle. The recordings of Figures 1 and 2 clearly show the distinction with respect to the prior art as discussed in WO95/01643 (Carnegie Mellon University), where such a complete surrounding is most clearly not on hand. Also, it must be taken into account here that in a recording in the transmission electron microscope the different parts of the preparation are imaged onto each other, as in a projection. Accordingly, the graphite layers visible in the electron microscope recording included in WO95/01643 are not necessarily in contact with the metal particle, but may be present above or under the metal particle. X-ray photoelectron spectroscopy can also be used to determine coverage with carbon. The photoelectrons coming from the metal are completely absent in the spectrum in the case of thicker layers, and are present to an attenuated extent in the case of thinner layers. Finally, the magnitude of the adsorption of hydrogen can be established to determine the extent of coverage of the surface of the metal particles with carbon. Little or no hydrogen is adsorbed onto the carbon surface, whereas the metal surfaces take up a great deal of hydrogen. For determining the accessible iron surface

of, for instance, ammonia synthesis catalysts, the chemisorption of carbon monoxide has been used for decades now. The magnitude of the amount of carbon monoxide chemisorbed at -78°C is calculated from the difference
5 between the total amount of adsorbed carbon monoxide and the reversibly adsorbed amount of carbon monoxide. On carbon surfaces no chemisorption of carbon monoxide occurs.

The thickness of the carbon layer can vary from about 1 nm to about 50 nm. As discussed above, the carbon layer
10 enveloping the ferromagnetic metal particles consists of layers of carbon atoms having a graphitic structure, with the stacking of the layers being less ordered than in the case of graphite. The fact that the graphitic layers are mutually ordered to a lesser extent than in graphite does not alter
15 the chemical stability of metal or alloy particles surrounded by such graphite layers.

The size of the carbon-covered ferromagnetic metal particles can be chosen within wide limits. It is possible to use carbon-covered particles having dimensions of about 4 nm
20 to 1 μm or more. With a view to different applications, it is of great significance that the size of the ferromagnetic particles can be properly controlled; it is then of importance that a relatively narrow particle size distribution of the ferromagnetic particles can be set.

25 The size of the ferromagnetic particles is especially relevant in the separation of the particles. Relatively large particles having dimensions of about 0.1 to 1 μm can be efficiently separated with a magnetic field of a relatively weak gradient. When it is not of importance to work with
30 extremely small particles having dimensions of, for instance, 30 nm, it will therefore be preferred to use ferromagnetic particles having a dimension of, for instance, 0.5 μm or more. In that case, no costly facilities are needed to apply a magnetic field with a strong gradient to the liquid phase.
35 Clearly, in that case the ferromagnetic material must not

contain any smaller magnetic particles, since these particles will not be separated then.

Smaller particles are attractive in, for instance, catalytic reactions, because then the number of particles
5 suspended in a unit volume of the liquid, per unit weight of the catalyst can be made high. In general, this leads to a higher activity. For the separation, however, a magnetic field with a strong gradient is then needed, which requires special provisions. When work is to be done with extremely
10 small particles, the presence of a few larger ferromagnetic particles is generally less objectionable. Accordingly, part of the invention is a mixture of relatively large ferromagnetic particles and much smaller ferromagnetic particles. Owing to the strong gradient of the magnetic field
15 around large ferromagnetic particles in an external magnetic field, it is also possible with a magnetic field without a strong gradient to separate (extremely) small ferromagnetic particles along with a small fraction of large ferromagnetic particles. The smaller ferromagnetic particles then
20 agglomerate around the large ferromagnetic particles. In that case, a suspended solid phase can be separated without utilizing an external magnetic field with a more or less strong gradient. The agglomerated particles generally sediment rapidly, while the agglomerates can also be
25 separated by filtration or centrifugation.

There are cases in which agglomeration of the carbon-covered ferromagnetic particles plays a less important role. Thus, when using the particles as electrode, the formation of clusters of particles is not important. Also, ferromagnetic
30 particles can be fixed in a particular area in a reactor with an inhomogeneous magnetic field and a flow of reactants can be passed therethrough. This makes it possible to use a pseudo fixed catalyst bed which contains much smaller catalyst bodies than a conventional fixed catalyst bed. When
35 in a conventional fixed catalyst bed the size of the bodies is made less than about 1 mm, the pressure drop over the

catalyst bed becomes too high, which causes channeling or results in the catalyst bed being pushed partly or wholly out of the reactor.

In other cases, however, and particularly in the use
5 as support for suspended catalysts, agglomeration of the ferromagnetic particles is disadvantageous. Thus, the activity of the suspended catalytically active particles decreases considerably through agglomeration. Agglomeration of suspended ferromagnetic particles is caused especially by
10 the permanent magnetic moment of small ferromagnetic particles. To prevent agglomeration of the ferromagnetic particles, it is therefore necessary that the ferromagnetic particles have no permanent magnetic moment.

Now, larger particles of ferromagnetic material have
15 no resulting permanent magnetic moment in that the material splits up into magnetic domains, the magnetic fields of which cancel each other out. However, if the ferromagnetic particles have dimensions in the order of magnitude of the thickness of the domain boundaries (the so-called Bloch
20 walls), the split-up into magnetical domains becomes energetically disadvantageous; below a particular size ferromagnetic particles occur as monodomains with a relatively strong external magnetic field. It is clear that in multidomain particles, agglomeration of the ferromagnetic
25 particles through magnetic interaction will not occur. It is therefore of great importance that the metal particles according to the invention have an isotropic form. Form anisotropy leads to monodomain particles which exhibit a relatively strong external magnetic field. With magnetic
30 tapes and disks for the storage of data, therefore, generally elongate magnetic particles are used to accomplish a high remanence. The dimensions at which monodomain behavior occurs in isotropic particles depend on the saturation magnetization and the magnetocrystalline anisotropy energy. The
35 magnetocrystalline anisotropy causes the energy of a magnetical domain or of a monodomain particle to vary with

the orientation of the magnetization with respect to the crystal lattice. This anisotropy derives from the spin orbit coupling. In isotropic iron particles, for the limit of monodomain behavior, a size of about 10 nm is specified. In
5 the case of nickel, the limit for monodomain behavior lies at larger particle dimensions, viz. in excess of 20 nm.

The magnetocrystalline anisotropy energy of a ferromagnetic particle is, of course, proportional to the volume of the particle. As a consequence, in the case of
10 extremely small particles which, owing to their small dimensions, consist of a single magnetical domain, the anisotropic energy can become of the order of the thermal energy. Through the coupling with the lattice vibrations, the orientation (not the magnitude) of the magnetic moment of
15 such particles now varies spontaneously, analogously to the Brownian movement of molecules and colloidal particles. According as the temperature is higher, the direction of the magnetic moment of a particle varies faster. Because the magnetic properties of such a collection of ferromagnetic
20 particles are analogous to those of a paramagnetic material having a very high atomic magnetic moment, the material is referred to in that case as a superparamagnetic material.

When properly dispersible, non-agglomerating ferromagnetic particles are required, therefore, according to
25 the invention multidomain particles are used or superparamagnetic particles. The presence of multidomain particles can be determined by measuring the remanence of the particles. For multidomain particles, this remanence lies below 30 to 40% of the saturation magnetization.
30 Superparamagnetic particles do not exhibit any remanence at all. Therefore, according to the invention, as properly dispersible bodies, ferromagnetic particles are used, the remanence of which is less than 30 to 40% of the saturation magnetization, preferably less than 20% of the saturation
35 magnetization, and more preferably less than 10% of the saturation magnetization.

By lowering the magnetocrystalline anisotropy energy, the limit below which monodomain behavior is exhibited can be shifted to smaller particles. Therefore, according to the invention, preferably alloys of a low magnetocrystalline anisotropy energy are used. In practice, with alloys of iron and nickel or of cobalt and iron, very low anisotropy energies can be obtained. Preferably, therefore, iron-nickel or iron-cobalt alloy particles according to the invention will be used. The preparation of iron-nickel alloys can be carried out according to the prior art as described hereinbelow for iron-cobalt alloys. In view of the high saturation magnetization of iron-cobalt alloys, this is an attractive combination. In view of the price of cobalt, however, it can often be more economic to work with iron-nickel alloys.

For the preparation of the ferromagnetic particles according to the invention, ferromagnetic particles of the desired metal or the desired alloy having the desired dimensions are provided on a support material conventional for heterogeneous catalysts, such as silicon dioxide, aluminum oxide or magnesium oxide. In this context, it is of importance that the reduction of metal oxides provided on support materials, according to the method of the present invention, leads to isotropic particles. For that matter, this is done in a manner known in the prior art, by providing optionally hydrated oxides of the desired metals on the support. It is most obvious to do this by impregnation of the support material with solutions of suitable salts of the metal to be provided or, in the case of alloys, of the metals to be provided. Both impregnation of the pore volume and impregnation with larger amounts of solution can be employed for this purpose. Coprecipitation of the support and the precursors of the desired ferromagnetic materials can also be applied according to the known prior art.

If it is desired to prepare ferromagnetic particles of a uniform size, the (hydrated) oxides must be applied

homogeneously over the surface of the support material. For this purpose, impregnation of the support material with solutions of salts of the metals to be applied is generally less satisfactory. According to the prior art, for realizing
5 a uniform distribution of the precursor over the support material, deposition-precipitation is eminently suitable. The dimensions of the resulting metal particles can be partly controlled by appropriately selecting the loading of the support material. For a lower loading of the support, and
10 hence for preparing small ferromagnetic particles, impregnation of the pore volume of the support material with suitable complexes of the metals to be applied, such as citrate and EDTA complexes, followed by drying and thermal decomposition of the complexes deposited on the support,
15 lends itself very well for obtaining a uniform distribution of the oxide over the support material.

After applying the oxide of the desired metal and removing the water, if any is present on the support, the oxide is reduced to the corresponding metal. Preferably, the
20 reduction is carried out by heating the loaded support in a flow of a hydrogen-containing gas mixture. While the reduction of nickel, because of the position of the thermodynamic equilibrium, is relatively simple, the reduction of cobalt and especially that of iron must be
25 carried out under properly controlled conditions. Especially in the reduction of iron, the water vapor pressure in the pores of the support must be kept low in the reduction. At too high a water vapor/hydrogen ratio, the reduction stops because of the position of the thermodynamic equilibrium at
30 magnetite, Fe_3O_4 . If the interaction with the support is strong, the reduction stops at wustite, FeO . According to the methods according to the invention, the reduction of the metal oxide provided on the support can also be carried out in a different way, with other reducing agents.

35 The dimensions of the resulting metal particles are determined by the loading of the support material, the

specific surface area of the support material, and the temperature at which the supported metal particles are eventually treated in a non-oxidizing environment. A high loading of a support with a relatively low specific surface area and a treatment at a high temperature naturally lead to large metal particles, whereas a low loading of a support with a relatively large specific surface area and treatment at a relatively low temperature result in small to very small metal particles.

Thereafter, the carbon layer is provided around the metal particles by exposing the supported metal particles at elevated temperature to a gas flow which contains carbon-containing molecules. With the exception of carbon dioxide, virtually all carbon-containing molecules that can be brought into gaseous form can be used for this purpose. The temperature needed for the decomposition of the carbon-containing molecules on the surface of the metals to form carbon layers naturally depends on the nature of the molecules. In the case of molecules such as benzene or toluene, relatively low temperatures may suffice, while in the case of carbon monoxide, by contrast, relatively high temperatures must be employed.

Finally, the support material is removed by treating the material pre-treated in the above-mentioned manner, with a suitable acid or base. Thus, an aluminum oxide or magnesium oxide support will preferably be removed by treatment with acid, although aluminum oxide can also be removed by treatment with lye. It has been found that the treatment with a non-oxidizing acid does not affect the metal completely surrounded by graphite layers, but solely dissolves the support. Silicon dioxide is preferably removed by treatment with lye.

Due to the above-described method of preparation, the magnetic material according to the present invention is essentially distinguished from the material described in Japanese patent application 02069904 published on 08-03-1990

in the name of Mitsubishi Petrochem Co. Ltd. In that publication, the starting material is a powder of metallic iron, cobalt or nickel or alloys of these metals. The particles of the powder have a size of 0.5 mm or less. Now, these particles are heated in a flow of carbon monoxide and hydrogen at a temperature of 150 to 400°C or in a flow of methane or ethane at a temperature of 300 to 500°C. Now, such metal particles must be processed to form mechanically strong agglomerates of a size of at least 1 mm to make it possible to pass a gas flow through a packed bed of the particles whereby all particles come into contact with the gas flow. For a fluidized bed, bodies of dimensions of at least 50 μ m are needed; smaller bodies are blown from the fluidized bed. Under reducing conditions, such agglomerates of particles, such as are to be used in a fixed bed or a fluidized bed, sinter very strongly. This holds in particular for nickel particles in the presence of carbon monoxide. Transport of nickel as nickel carbonyl then leads to a very strong and rapid sintering. In the manner described, it is therefore not possible to obtain small graphite-covered metal particles.

When ferromagnetic particles with a very high saturation magnetization are desired, it is attractive to use iron and in particular iron-cobalt alloys as ferromagnetic component. When ferromagnetic particles with a permanent magnetic moment are desired, which can be used while mixed with smaller ferromagnetic particles, alloys of cobalt and iron with a high content of cobalt are attractive. For magnetic soft material having a low permanent magnetic moment of the individual particles, and hence a low remanence, cobalt-iron alloys with a lower cobalt content and nickel-iron alloys are suitable. According to the invention, in the above-mentioned cases, a mixed oxide of iron and cobalt or of iron and nickel is provided on the support. According to the known prior art, this is possible by injection of an acid iron ion- and cobalt ion-containing solution or an acid iron ion- and nickel ion-containing solution into a suspension of

the desired support in an aqueous solution, the pH of which is held at a value above about 5 through simultaneous injection of an alkaline solution. According to the known prior art, this is also possible by suspending the support in a solution of cobalt(II) and iron(II) ions or of nickel(II) and iron(II) ions, to which ammonium nitrate and urea have been added. Upon heating, the iron(II) is oxidized by the nitrate ions to iron (III), which hydrolyzes and precipitates with the cobalt or with iron(II) as CoFe_2O_4 and $\text{Fe(II)Fe(III)}_2\text{O}_4$. The hydrolysis of urea leads to (bi)carbonate ions which react with the hydrogen ions being released. In this way, the pH is maintained at the desired level. Obviously, the pH can also be adjusted to the desired value by injection of an alkaline solution. Both of the above-mentioned procedures yield particles of a uniform composition, while the precipitated material is homogeneously distributed over the (internal) surface of the suspended support, provided that the porous support particles are not greater than approximately 3 μm . Owing to the transport through the longer pores, the suspended support bodies are then loaded more heavily at the edge than in the interior. Such preparation methods are described in the patent applications South-Africa 6804216 of 18 November 1968, Netherlands 6804511 of 2 October 1969, Netherlands 6804970 of 9 April 1968, Netherlands 6815906 of 8 November 1968, German Offenlegungsschrift 1958606 of 18 June 1970, Ger.Offen. 1963828 of 8 October 1970, Ger.Offen. 2000321 of 16 July 1970, Netherlands 6904043 of 17 September 1970, British Patent Specification 1346498 of 13 February 1974. All these patent applications are in the name of Stamicarbon N.V.

According to a preferred method according to the invention, particles of iron or of alloys of cobalt and iron or of nickel and iron or of all three metals mentioned, are prepared starting from complex cyanides of iron. Iron particles are obtained according to the preferred method by precipitating complex iron cyanides by addition of dissolved

iron(II) compounds to, for instance, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6$.
Precipitation of complex iron cyanides, having as the
tetravalent or trivalent anion $\text{Fe}(\text{CN})_6$, or having $\text{Fe}(\text{CN})_5(\text{NO})$
as anion with nickel and/or cobalt, makes it possible to
5 prepare small alloy particles of a uniform chemical
composition. The reduction of such complex cyanides proceeds
very readily. If it is desired to prepare small alloy
particles, the cyanides, prior to the reduction to the alloy,
must first be converted into the corresponding mixed oxides
10 by calcining in an oxidizing gas flow. Large alloy particles
are obtained by immediately heating the complex cyanides
provided on a support in a reducing gas flow. Analysis of the
chemical composition of the resulting individual alloy
particles in the electron microscope has demonstrated that a
15 highly uniform chemical composition of the particles is
obtained.

The particles according to the invention can be
employed with much advantage for a number of technically
important processes. As discussed above, the most obvious
20 application is as support for catalytically active materials.
It is also possible to adsorb compounds or elements onto the
carbon surface and subsequently separate those with the
particles. It is further possible to provide certain protein
molecules on the carbon surface and subsequently to separate
25 the magnetic particles or determine the location of the
magnetic particles with a magnetic sensor.

Often, it is attractive to enlarge the surface
available for applying catalytically active components.
According to the invention, this is done by having small
30 clusters of carbon fibrils grow out of the ferromagnetic
metal particles provided on a support. 'Small' in this
connection is understood to mean a diameter of the clusters
of carbon fibrils of less than 3 μm . The growth is stopped by
abruptly raising the temperature to which the supported metal
35 particles are subject in a gas flow containing molecules with
carbon atoms. In this way, short carbon fibrils can be grown

from the metal particles and subsequently the metal particles can be encapsulated in carbon. After growth of the carbon fibrils and encapsulation of the metal particles, the support material on which the metal or alloy particles had originally
5 been provided is removed. Because of the high electric conductance of the carbon fibrils, this material is very attractive for use as electrodes. Such clusters of carbon fibrils are also highly suitable as support for suspended catalytically active materials. Separation by magnetic route
10 is eminently possible with such clusters of carbon fibrils in which one or more ferromagnetic particles are present.

According to the prior art, it is known to grow mechanically strong carbon fibrils, with the graphite layers oriented parallel to the fibril axis. Such carbon fibrils and
15 the preparation thereof are disclosed, for instance, in U.S. 5,171,560 in the name of Hyperion Catalyst International. In addition, it is possible to grow carbon fibrils where the graphite layers are oriented at an angle to the fibril axis, see U.S. 4,855,091 8 August 1989 in the name of DOW Chemical.
20 If such an orientation of the graphite layers is involved, this is sometimes referred to as a fishbone structure.

Now, the mechanical strength of *thin* carbon fibrils with a fishbone structure is lower than that of carbon fibrils where the graphite layers are oriented parallel to
25 the fibril axis. What is meant in this connection by the mechanical strength is particularly the tensile strength; the compression strength of the two kinds of carbon fibrils does not differ appreciably. 'Thin' in this case means a diameter of the fibril of about 50 nm at a maximum. Surprisingly,
30 however, thick carbon fibrils having a fishbone structure prove to have a mechanical strength which is considerably higher than that of fibrils having a parallel orientation of the graphite layers, which can only be grown as thin fibrils. In this connection, a thick carbon fibril is a fibril having
35 a diameter of about 50 nm or more. An advantage of carbon fibrils having a fishbone structure is that the surface

contains more reactive sites than the surface of carbon fibrils where the graphite surfaces are oriented parallel to the fibril axis. Also, potassium can be intercalated in such fibrils, which opens a number of application possibilities of interest.

According to the invention, mechanically strong bodies of carbon fibrils are obtained by growing carbon fibrils with a fishbone structure of a diameter of at least about 50 nm. Such thick fibrils are generally not straight, but highly tortuous. The interweaving of the fibrils thereby caused leads to a high mechanical strength of the clusters of carbon fibrils. Accordingly, such bodies of carbon fibrils having a fishbone structure form part of the invention. The size of the bodies can be governed by controlling the time during which the carbon fibrils grow. By abruptly increasing the thermodynamic potential of the carbon in the gas atmosphere, the metal particles from which the carbon fibrils grow encapsulate, so that growth stops. In this way, it is possible to grow bodies of dimensions of less than 1 μm to a few mm's or more.

Accordingly, the above-mentioned special form of the material according to the invention also encompasses mechanically strong clusters of carbon fibrils having a fishbone structure, while the size of the clusters is greater than 3 μm . The content of ferromagnetic material is then much lower than in the materials discussed earlier. When the clusters are allowed to grow to dimensions of 3 μm or more, actually no magnetic material is needed for separation, since the clusters can then be readily separated by sedimentation, filtration or centrifugation. It is possible to have the growth of the carbon fibrils proceed such that the ferromagnetic material is hardly, if at all, encapsulated. Subsequently, the magnetic material can be removed, if desired, by dissolving in acid. In general, however, it will be preferred to encapsulate the metal or alloy particles.

For certain applications, however, the accessible surface and the pore volume of thick carbon fibrils having a fishbone structure may be too small. Then, according to a special embodiment of the present invention, bodies are used which contain both thin and thick carbon fibrils, while the thin carbon fibrils can have the graphite layers oriented both parallel to the fibril axis and at an angle, and the thick carbon fibrils have a fishbone structure. The accessible surface and the pore volume are then provided by the thin fibrils and the mechanical strength by the thick carbon fibrils. According to the present invention, such clusters of thin and thick carbon fibrils having a fishbone structure are produced by starting from support materials conventional in solid catalysts, which are loaded with metal or alloy particles of different dimensions. Naturally, metal or alloy particles of different dimensions can also be obtained by mixing two support materials each loaded with more or less uniform metal or alloy particles which differ appreciably for the two supports. According to the invention, the starting material are metal or alloy particles of more than 30 nm and of less than 20 nm. From the work of Hoogenraad (M. Hoogenraad "Growth and Utilization of Carbon Fibrils" Dissertation University of Utrecht, 1995) it is known that at a high temperature, for instance at 600°C, from a mixture of carbon monoxide and hydrogen, selectively thin carbon fibrils can be grown from the small metal or alloy particles. If subsequently the temperature is decreased to 500°C, mechanically strong thick fibrils are grown from the large metal or alloy particles.

A special embodiment of the material according to the invention comprises mechanically strong clusters of carbon fibrils, while the size of the clusters is greater than 3 μm . For the mechanical strength, these clusters contain thick carbon fibrils, the graphite layers of which are ordered according to a fishbone structure. If a large surface and/or pore volume is desired, thin carbon fibrils with graphite

layers ordered parallel or according to a fishbone structure are incorporated into the clusters. The content of ferromagnetic material is then much lower than in the materials discussed earlier. When the clusters are allowed to grow to dimensions of 3 μm or more, there is even no magnetic material needed for the separation, since the clusters can then be readily separated by sedimentation, filtration or centrifugation. It is possible to have the growth of the carbon fibrils proceed such that the ferromagnetic material is hardly, if at all, encapsulated. Subsequently, the magnetic material can be removed, if desired, by dissolving in acid. In general, however, it will be preferred to encapsulate the metal or alloy particles.

According to a special method according to the present invention, a mixture of small and large supported metal or alloy particles is obtained by preparing the starting materials separately. By high-loading a support with a precursor of the metal or the alloy, large particles are obtained, after reduction, while a low loading leads to small particles. A condition is that in both cases the support is uniformly loaded with the active precursor. According to the known prior art, a number of methods are known for this purpose, such as deposition-precipitation or impregnation with citrate complexes.

To obtain a proper mixing of the support particles loaded with the precursor to different extents, the starting point is conglomerates of support particles not greater than 1 mm, preferably not greater than 0.5 mm and more preferably not greater than 0.2 mm. After the loading with the precursor of the metal or the alloy, the support particles are suspended in a liquid, preferably in water, whereafter the suspension is properly mixed. After separation of the liquid and drying and, if necessary, calcining, the loaded support particles are formed into bodies of the dimensions desired for the growth of carbon fibrils.

The desired ratio of thick and thin carbon fibrils is determined by the desired surface area and pore volume and the required mechanical strength. According to the invention, the mass ratio of large and small metal particles is varied
5 from about 2:1 to 1:100.

According to the invention, as mentioned above, for large surfaces and large pore volumes, a mixture of fibrils having a fishbone structure and a parallel structure can be prepared. Such mixtures are therefore also part of the
10 invention. In this case, a metal or alloy is selected from which, under specified conditions, fibrils having a fishbone structure grow, such as, for instance, nickel, and a metal or alloy from which parallel fibrils grow, such as, for instance, iron. For that matter, under different conditions,
15 during growth, fibrils having a parallel orientation of the graphite layers can be grown from nickel particles. A mixture of nickel- and iron-loaded support particles is prepared according to the invention as described above. In this way, it is possible to combine the chemical reactivity and
20 mechanical strength of fibrils having a fishbone structure, with the large pore volume of fibrils having a parallel orientation of the graphite layers. According to the invention, the mass ratio of the metal particles that grow thick carbon fibrils having a fishbone structure and thin
25 carbon fibrils having a parallel structure is likewise varied from about 2:1 to about 1:100.

The carbon fibrils having a fishbone structure prove to have a high electric conductance. This conductance has been established by providing the carbon fibrils on an
30 aluminum table as used in scanning electron microscopy. In the scanning electron microscope, a low conductance of a preparation leads to local charging of the preparation at those positions where contact with the aluminum of the preparation table is poor. By the electrons incident on the
35 preparation, the parts of the preparation that make poor contact with the aluminum preparation table are negatively

charged. As a consequence, the electrons are incident on the negatively charged parts of the preparation at a lower velocity. The intensity of the secondary electrons increases strongly with decreasing energy of the incident electrons. In the picture of the secondary electrons, the negatively charged parts of the preparation are thus recognizable by a much higher intensity of the secondary electrons. Charging of the carbon fibrils would then appear from a strong difference in intensity of the secondary electrons stemming from different parts of the preparation. Also in the case of a thick layer of carbon fibrils, where contact with the aluminum table is much less, not any charging is found to occur, which points to a high conductance of the carbon fibrils. This is illustrated in Figure 3, which represents a recording at a high magnification in a scanning electron microscope equipped with a field emission electron gun. A high electric conductance may also be theoretically expected from the structure of the carbon fibrils, which consist of graphite layers.

Thick carbon fibrils having a fishbone structure or the above-described mixture of thick and thin carbon fibrils are found to be very well processable in polymers. According to a special form of the material according to the invention, polymers are therefore obtained having an electric conductance considerably higher than that of the pure polymer, by processing into the polymers carbon fibrils having a fishbone structure or a mixture of intertwined thick carbon fibrils having a fishbone structure and thin carbon fibrils having a parallel or fishbone structure. Such processing is done by the use of techniques known per se, such as, for instance, master batching, or mixing the carbon fibrils with the polymer powder, followed by extrusion. The invention therefore encompasses polymers into which carbon fibrils having a fishbone structure have been processed.

Hereinabove, the use as support for catalytically active materials has been mentioned. According to a special

embodiment of the present invention, therefore, the material is used as support for catalytically active components. In this case, a (precursor of a) catalytically active material is provided on the carbon surface. For providing active
5 components, methodologies can be used which are known according to the prior art for providing (precursors of) catalytically active materials on activated carbon.

Now, a part of the large internal surface of activated carbon oxidizes relatively rapidly upon exposure to the air.
10 As a consequence, the surface of activated carbon after exposure to the air for about 24 hours contains many polar groups, such as carboxyl groups, to which precursors of catalytically active materials adsorb strongly. Accordingly, after exposure to the air, activated carbon is hydrophilic.
15 To such polar groups, (precursors of) active components can be readily adsorbed and thus catalytically active materials can be provided on the surface of activated carbon. The surface of the carbon layers according to the invention oxidizes much less fast. Indeed, the encapsulated
20 ferromagnetic particles and the (clusters of) carbon fibrils are hydrophobic. Through a mild oxidation, a limited number of carboxyl groups can be provided on the surface on the material according to the present invention, to which positively charged (precursors of) active components, such as
25 ammonia complexes of noble metals, can be adsorbed. A mild oxidation can be performed, for instance, according to the prior art by suspending the encapsulated particles in diluted nitric acid and boiling for a short time. According to the prior art, other mild oxidation procedures, such as oxidation
30 with hypochlorite, are also known. Upon prolonged boiling, the typically thin carbon layer is oxidized completely and the metal or alloy particles dissolve. Eminent results are also obtained by reducing dissolved compounds of noble metals, preferably complexes with ammonia or amines, in the
35 liquid phase in the presence of suspended encapsulated particles. A very fine distribution of the active metal

results when the reduction is performed at a temperature lower than that at which the reduction in the liquid phase in the absence of suspended encapsulated particles proceeds. Often, it is attractive to provide somewhat larger noble metal particles on the carbon fibrils. According to a special method according to the invention, this is done by loading mildly oxidized fibrils with a relatively small amount of a (precursor of an) active component. In general, such a loading is below 2% by weight and after reduction metal particles are obtained having dimensions of about 1 nm. By carrying out the reduction in the presence of a dissolved precursor of the active element under conditions where the reduction in the liquid phase proceeds while being exclusively catalyzed by the small particles already provided, the primarily provided catalytically active particles can be selectively grown into larger particles. By providing a different compound on the primarily provided particles, it is possible in this way to also provide active materials consisting of several components with a uniform composition of the active particles.

When a higher loading with metals that can be reduced at a low temperature is desired, a preferred method according to the invention is used. In that case, the carbon fibrils are impregnated with a solution of sugar or glucose, after which the impregnated carbon fibrils are dried. Then the resultant layer of sugar is decomposed at elevated temperature in an inert gas or an inert gas flow. What is then obtained is a thin, strongly adherent layer of amorphous carbon on the carbon fibrils having an oxygen content depending on the decomposition temperature. This layer oxidizes fast upon exposure to atmospheric air, so that hydrophilic fibrils are obtained, which strongly adsorb complexes, for instance chloride complexes, of, for instance, noble metals. The noble metals can be reduced in an aqueous phase with formaldehyde or glucose or by passing hydrogen through the suspension.

According to a preferred mode of the invention, precursors of active components are provided on the surface of the materials according to the invention by impregnation with solutions of complexes of organic compounds, such as
5 EDTA or citric acid. It is also possible first to provide surface-active compounds on the surface of the materials according to the present invention and then to provide the active components on the pre-treated surface. Often, the precursors of the active component(s) can advantageously be
10 added to a solution of glucose or sugar. Upon drying of materials impregnated with such solutions, a viscous layer is formed on the carbon surface of the materials according to the present invention. According to the prior art, the organic material is removed by heating the loaded support
15 material in an oxygen-containing gas or an oxygen-containing gas flow. Such a method cannot be used with the support materials according to the present invention, since in that case the carbon is also oxidized from the support. This holds the more so since the (precursors of the) catalytically
20 active materials in general also catalytically accelerate the oxidation of the carbon fibrils and carbon layers of the material according to the present invention.

According to the invention, the organic ingredients of the impregnated material are removed by heating the loaded
25 supports in an inert gas flow at a high temperature. The catalytically active components then generally remain behind, together with residues with a high carbon content, which largely cover the active components. By treatment with hydrogen at elevated temperature, the carbon-containing
30 residues can be removed. Typically, such carbon-containing supports, such as the support materials according to the present invention, will be used as support for metallic active components. In that case, also a reduction treatment is necessary to convert the precursor(s) of the active
35 component(s) to the corresponding metals or alloys. Now, noble metals can be reduced at a very low temperature, at

which the carbon of the support does not react. However, when higher temperatures are necessary for reduction, as with cobalt and iron, also the carbon of the support will react to form methane. Reduction is therefore necessary both for the
5 impregnation with complexes of organic compounds and for the reduction of less noble metals or alloys.

In the case of noble metals, heating in an inert gas flow, such as argon or nitrogen, nearly always suffices. In that case, the metal is at least partly reduced by the carbon
10 of the fibrils. In general, this involves only a relatively minor amount of carbon. Therefore, according to a special embodiment of the method according to the invention, noble metal precursors provided on the carbon fibrils are reduced by heating in an inert gas or an inert gas flow.

15 Surprisingly, it has now been found that when the hydrogen and methane partial pressure is set at such a value that the value of $p_{H_2}^2/p_{CH_4}$ lies between the value for the equilibrium between the metal carbide, hydrogen and methane and that between graphite, hydrogen and methane, neither
20 hydrogenation of carbon to methane nor formation of metal carbide arises. Also for the equilibrium between carbon monoxide, carbon dioxide and graphite or the metal carbide, such a behavior has been found. According to a special embodiment of the method according to the invention,
25 therefore, the reduction is carried out under such conditions that neither the equilibrium between graphite nor that between the metal carbide and the corresponding gas molecules can be attained.

Support materials according to the invention are
30 particularly attractive as supports of catalytically active materials for hydrogenating desulfurization, denitrogenation or the hydrogenating removal of metals from crude oil fractions. In general, cobalt and molybdenum containing catalysts are used for hydrogenating desulfurization, while
35 nickel and tungsten catalysts are suitable for removing nitrogen from petroleum fractions. A great advantage of

support materials according to the invention is that in the spent catalysts the carbon support can be readily oxidized off. The residual components can then be processed comparatively easily, in contrast to catalysts according to the prior art, where aluminum oxide is used as support. Processing the relatively large amount of aluminum oxide is cumbersome. It has now been found that molybdenum(III) chloride is not properly taken up by the carbon fibrils or by the carbon layers deposited on the ferromagnetic particles, but that, surprisingly, the molybdenum, after oxidation, is strongly sorbed. After sulfurizing the carbon fibrils loaded with cobalt or nickel and molybdenum, extremely active catalysts are obtained. Because of the large pore volume and the open pores of the clusters of carbon fibrils, the thus obtained catalysts are eminently suitable for processing heavier, metal-containing oil fractions. Keeping catalytic particles magnetically in suspension or magnetically separating catalytic particles is also applicable with great advantage in the processing of petroleum fractions. Especially in the hydrogenating demetallization, carbon fibrils loaded with sulfides are attractive. Here, especially nickel and vanadium are deposited on the catalyst. The spent catalysts can be technically simply processed by oxidizing the carbon fibrils completely. The remaining cobalt or nickel and the vanadium and molybdenum can then be readily recovered. As a result, the work-up of carbon-supported catalysts can proceed much faster than that of the catalysts with aluminum oxide as support according to the prior art.

According to a special embodiment of the invention, Ziegler-Natta catalysts are provided on clusters of carbon fibrils. In particular the chlorides, such as, for instance, TiCl_3 , can be eminently provided on carbon fibrils grown from metal particles. When a relatively high loading with titanium trichloride is contemplated, pretreating the carbon fibrils with Cl_2 at elevated temperature is recommendable. It is also possible to provide a thin layer of amorphous, oxygen-

containing carbon by decomposing glucose or sugar, as described above. If carbon fibrils loaded in such a manner are used for polymerizing olefins, olefins are obtained of a sufficient electric conductance to prevent electrostatic
5 charging. Also metallocenes can be provided on the carbon fibrils and in this way suitable polymerization catalysts can be obtained.

Of great interest is that it is also possible to provide thin layers of zeolites for use as acid catalysts on
10 the carbon fibrils according to the invention. In that case, a surface-active substance is provided on the surface of the carbon fibrils, whereafter the pretreated carbon fibrils are introduced in a synthesis suspension of zeolites. A great advantage is that in this way a large area to volume ratio of
15 the zeolite is realized, so that transport impediments are entirely avoided. In liquid phase reactions it is often cumbersome to separate the small zeolite crystallites, after reaction, from the liquid. With zeolite layers provided on carbon fibrils according to the present invention, separation
20 of the zeolites from the liquid can be very readily effected by filtration or centrifugation. If desired, the carbon fibrils, after loading with the zeolite, can be burnt away. Now, the inner surface of the zeolite layer is also accessible from the gas or the liquid phase. The mechanical
25 strength of the system, however, is then less.

A drawback of the carbon fibrils according to the present invention is that the fibrils are not resistant to an oxidizing environment at elevated temperature. According to a special embodiment of the invention, the carbon fibrils are
30 therefore converted into silicon carbide fibrils. At the surface of silicon carbide a sealing layer of silicon oxide is formed, which prevents further oxidation. The conversion of the carbon fibrils to silicon carbide can be carried out according to the known prior art. Preferably, the fibrils are
35 heated in a flow of silicon monoxide. The relatively volatile silicon monoxide is obtained by heating silicon with silicon

dioxide. Carbon fibrils converted to silicon carbide in this way are, according to the invention, an excellent catalyst support. According to the known prior art, also volatile halogen silanes can be used for the reaction to silicon
5 carbide.

The carbon fibrils according to the invention, whether or not combined with ferromagnetic particles, form an excellent support for ion exchangers. The large pore volume and the wide pores render this material eminently suitable
10 for providing ion exchangers. According to the prior art, ion exchangers can be obtained by mild oxidation, which leads to the presence of carboxyl groups on the carbon surface. More strongly acid ion exchangers can be obtained by reaction with sulfuric acid, as is known according to the prior art for
15 carbon. Also, known ion exchangers can be provided on the surface of the materials according to the invention. In particular ion exchangers based on polystyrene are suitable for provision on the carbon fibrils. For strongly acid catalysts that can also be used at relatively high
20 temperatures, Nafion can be provided on the materials according to the invention.

The carbon fibrils thus loaded with ion exchangers can be used well in a fixed bed, whereby a great fraction of the ion exchanging groups can be utilized. It is also possible to
25 suspend the loaded fibrils and subsequently separate them through filtration or centrifugation. Highly attractive is the use of clusters of carbon fibrils in which encapsulated ferromagnetic particles are present which can quite readily be kept suspended in a flowing liquid or can be very easily
30 separated by applying a magnetic field.

Carbon fibrils loaded with ion exchangers are eminently applicable as acid catalysts. The poor transport properties of the ion exchangers according to the conventional prior art and the relatively low thermal
35 stability are strongly improved by their provision on carbon fibrils.

In technical applications of support materials for catalytically active materials, the pressure drop over the reactor is often of critical importance. The pressure drop is determined by the size of the bodies of the catalyst. In
5 general, in a fixed catalyst bed, bodies of at least a few mm will be used to keep the pressure drop within acceptable values. Also when using ion exchangers in a fixed bed, it is of significance to use sufficiently large bodies. According to the invention, bodies of dimensions of a few mm's or more
10 are then grown from the support materials loaded with metal or alloy particles. In that case, the conditions during the growth of the carbon fibrils are set such that relatively long thick carbon fibrils grow.

Surprisingly, it has further been found that also
15 bodies of a few mm's chiefly consisting of carbon fibrils can be obtained by starting from bodies of a suitable catalyst support, such as aluminum oxide or silicon oxide, of a few mm's. On the (internal) surface of these porous particles, the metal particles are provided from which it is desired to
20 grow the carbon fibrils. Now, if the carbon fibrils are then allowed to grow, mechanically strong bodies having slightly greater dimensions than the original support bodies are obtained. According to the invention, bodies are used then which consist of conventional catalyst supports in which
25 carbon fibrils have been grown which at the same time cover the external surface of the original support particles. According to the invention, such support particles are obtained by providing support bodies with metal particles of dimensions between about 5 nm and 0.2 mm and growing carbon
30 fibrils therefrom.

Part of the invention are electrodes obtained by introducing metal particles covered with carbon layers or carbon fibrils coupled to encapsulated metal particles, into a magnetic field, which keeps the particles oriented
35 according to the lines of magnetic force. Owing to the gradient of the magnetic field, the particles are held at the

desired position, while further a good contact between the particles is obtained. The electric conductance of the ferromagnetic metals is high, as is that of the carbon layers and the carbon fibrils. In this way, a well conducting electrode having a high specific surface is obtained. Another application of ferromagnetic particles completely covered with graphitic carbon layers is as electrode for electrochemical reactions. In certain cases, no other active components need to be provided on the carbon surface then.

It has been found that such an electrode is eminently suitable for the electrochemical production of diluted hydrogen peroxide solutions.

EXAMPLES

Example 1 Preparation of nickel iron oxide on aluminum oxide

To a suspension of 4.3 g of nickel nitrate and 5.0 g of γ -aluminum oxide in 1.5 l demineralized water, there was added a solution of 2.1 g of ammonium ferrocyanide in 100 ml demineralized water at a rate of 1 ml/min. The pH of the solution was pre-set at 5. After complete addition of the cyanide solution, the suspension was filtered off, washed and dried. A molar fraction of 425 μm to 825 μm was calcined in a flow of 20% O_2 in He (total flow 100 ml/min) at 573 K for 3 hours. Characterization was done through XRD.

Example 2 Preparation of isolated iron nickel particles

100 Milligrams of a nickel iron oxide on γ -aluminum oxide were reduced *in situ* in a gas flow of 20% H_2 (in Ar, total flow 100 ml/min) in a reactor especially designed therefor. The temperature was raised to 973 K and held at this value for 2 hours. Then encapsulation occurred by replacing H_2 with CH_4 , and passing this gas through at 973 K

for one hour. After complete encapsulation had occurred, the material was cooled off to room temperature under an argon flow. Then the γ -aluminum oxide was removed by boiling the preparation in 50 ml of concentrated hydrochloric acid for 8
5 hours. The isolated encapsulated iron nickel particles were characterized with TEM.

Example 3 Use of magnetic support particles for the hydrogenation of cyclohexene

10

0.12 Grams of iron nickel particles encapsulated analogously to those described in Example 2 were impregnated with 0.11 ml of an acid palladium chloride solution. The concentration of the palladium chloride solution was 0.25
15 molar. The impregnated support was dried at 60°C in a flow of argon. Then the palladium was reduced at the same temperature by mixing 10 vol.% of hydrogen in the argon flow. As appears from examination in the transmission electron microscope, small palladium particles had been deposited on the carbon
20 shells around the ferromagnetic particles. The dimensions of the palladium particles were about 1 to 2 nm.

The catalyst was suspended in toluene, whereafter hydrogen was passed through to reduce again the palladium particles oxidized in the air. Then cyclohexene was injected
25 into the suspension. The hydrogenation rate was determined by measuring the hydrogen consumption. The hydrogen consumption was compared with that of a commercial palladium catalyst with activated carbon as support. Although the palladium content of the magnetic support according to the invention
30 was half of that of the commercial catalyst, the hydrogenation rate was equal.

Example 4 Preparation of expanded spherical support particles

35 The starting material were spherical particles of aluminum oxide of dimensions between 1 and 0.85 mm. By

impregnation of the pore volume with an aqueous nickel nitrate solution and subsequent drying at 115°C and calcining at 450°C, nickel oxide particles of a wide particle size distribution were provided in the spherical support bodies.

5 Then the support particles thus loaded with nickel oxide were reduced in a flow of hydrogen at 450°C, yielding metallic nickel particles of particle dimensions varying from 3 to 50 nm.

Thereafter the reduced support bodies, without interim
10 exposure to the air, were exposed at 450 to 500°C to a flow of methane and hydrogen in a ratio of 1:2. After about one hour, it was found that the diameter of the support particles had increased to about 1.3 mm. Examination in the electron microscope revealed that carbon fibrils of a strongly varying
15 diameter had grown from and in the support particles.

The mechanical strength of the spherical support bodies from which the carbon fibrils had grown was found not to have decreased materially, as appears from a test in which the sidecrushing strength was determined.

20

Legends to the figures

25 Figure 1 Encapsulated iron-nickel particle at a low magnification. Recording in the transmission electron microscope.

Figure 2 Encapsulated iron-nickel particle at a very high magnification. (a) iron-nickel particle; (b)
30 graphitic layers. Distance between the graphitic layers 0.33 nm

Figure 3 Recording made with a scanning electron microscope equipped with a field emission electron gun, of a thick layer of carbon fibrils having a fishbone
35 structure.

Claims

1. Ferromagnetic metal particles comprising a core of a ferromagnetic metal or metal alloy, wherein the surface of said core is covered entirely with a layer of graphitic carbon.
- 5 2. Particles according to claim 1, wherein the thickness of the graphitic carbon layer is between about 1 and about 50 nm.
3. Particles according to claim 1, wherein the maximum dimension is between 4 nm and 5 μm , preferably between 4 nm and 1 μm .
- 10 4. Particles according to claims 1 through 2, with dimensions of the ferromagnetic phase of at least 0.5 μm , while no smaller particles are on hand.
5. Particles according to claims 1 through 2 with such a bimodal distribution of dimensions of the ferromagnetic phase that side by side (a smaller fraction of) particles having dimensions of at least 0.5 μm and (a larger fraction of) particles having dimensions of maximally 0.1 μm are present.
- 15 6. Particles according to claims 1 through 5, wherein the dimensions of the individual ferromagnetic cores are substantially the same in all directions.
- 20 7. Particles according to claims 1 through 6, wherein the ferromagnetic phase of the particles is either multidomain or superparamagnetic.
- 25 8. Particles according to claims 1 through 7, wherein the remanence magnetization is not higher than 40%, preferably 20% and more preferably 10% of the saturation magnetization.
9. Particles according to claims 1 through 7, wherein the ferromagnetic phase consists of an iron-cobalt or an iron-nickel alloy.
- 30 10. Preparation of carbon-covered ferromagnetic metal particles according to claims 1 through 9 by loading a

support material with a (hydrated) oxide of the desired metal, drying and calcining the loaded support material and subsequently reducing the metal oxide to the corresponding metal or the corresponding alloy, whereafter a carbon layer
5 is provided on the metal particles by treating the material at elevated temperature in a gas flow which contains carbon-containing molecules, finally after cooling of the thus treated material the support material is dissolved.

11. Preparation of carbon-covered ferromagnetic metal
10 particles according to claim 10, wherein as support material, silicon dioxide, aluminum oxide or magnesium oxide is used.

12. Preparation of carbon-covered ferromagnetic metal particles according to claims 10 and 11, wherein the hydrated metal oxide is provided on the support by deposition-
15 precipitation.

13. Preparation of carbon-covered ferromagnetic metal particles according to claims 10 and 11, wherein the metal oxide is provided on the support through a pore volume impregnation with an EDTA or citrate complex of the desired
20 metal and this complex is subsequently decomposed at elevated temperature in an oxidizing gas flow.

14. Preparation of carbon-covered ferromagnetic metal particles according to claims 10 through 13, wherein the reduction of the supported metal oxide is carried out at a
25 high temperature in a flow of a hydrogen-containing gas mixture.

15. Preparation of carbon-covered ferromagnetic metal particles according to claims 10 through 14, wherein the covering with carbon is carried out by exposing the material
30 at elevated temperature to a gas flow with benzene, toluene, acetylene, ethylene, methane or carbon monoxide, to which, if necessary, hydrogen has been added.

16. Preparation of carbon-covered ferromagnetic metal particles according to claims 10 through 14, wherein the
35 support material is dissolved in an aqueous solution of a

non-oxidizing acid, such as hydrochloric acid, formic acid or acetic acid.

17. Preparation of iron particles according to claims 1 through 11 by precipitating complex iron cyanides in the presence of a support material suspended in the liquid by mixing solutions of iron(II) and of the tetravalent or trivalent anion $\text{Fe}(\text{CN})_6$, wherein, for preparing small iron particles, the cyanides, prior to the reduction to the alloy, are first converted to the corresponding oxides by calcining in an oxidizing gas flow and, for preparing large iron particles, the complex cyanides provided on a support are immediately heated in a reducing gas flow.

18. Preparation of alloy particles of cobalt and iron or of nickel and iron or of all three said metals according to claims 1 through 11 by precipitating complex cobalt-iron or cobalt-nickel or cobalt-nickel-iron cyanides in the presence of a support material suspended in the liquid by mixing solutions of nickel and/or cobalt and, if necessary, iron(II) and of the tetravalent or trivalent anion $\text{Fe}(\text{CN})_6$, or of $\text{Fe}(\text{CN})_5(\text{NO})$ as anion, wherein, for preparing small alloy particles, the cyanides, prior to the reduction to the alloy, are first converted to the corresponding mixed oxides by calcining in an oxidizing gas flow and, for large alloy particles, the complex cyanides provided on a support are immediately heated in a reducing gas flow.

19. Clusters of carbon fibrils of a maximum dimension of about 3 μm , in which one or more ferromagnetic particles are present.

20. Carbon fibrils with a fishbone structure having a diameter of more than about 50 nm.

21. Bodies of carbon fibrils with a fishbone structure having a diameter of at least about 50 nm.

22. Bodies of carbon fibrils with a fishbone structure according to claim 21 in which no ferromagnetic particles are present.

23. Clusters of carbon fibrils with a fishbone structure according to claims 20 through 22, wherein the dimension of the clusters is greater than 3 μm .
24. Bodies containing both thin and thick carbon fibrils, wherein the thin carbon fibrils can have the graphite layers oriented both parallel to the fibril axis and at an angle, and the thick carbon fibrils exhibit a fishbone structure.
25. Preparation of clusters of thin and thick carbon fibrils according to claim 24 by starting from support materials conventional in solid catalysts, which are loaded with metal or alloy particles of different dimensions.
26. Clusters of carbon fibrils grown from mixtures of supported metal or alloy particles consisting of particles greater than 30 nm and smaller than 20 nm.
27. Clusters of carbon fibrils according to claim 26, wherein the mass ratio of the greater and the smaller particles is between 2:1 and 1:100.
28. Clusters of carbon fibrils according to claims 25 through 27 grown from metal or alloy particles of different dimensions provided on support bodies which are not greater than 1 mm, preferably not greater than 0.5 mm and more preferably not greater than 0.2 mm, which after loading with the precursor of the metal or the alloy are suspended in a liquid, preferably in water, whereafter the suspension is properly mixed, which after separation from the liquid and drying and, if necessary, calcining, are formed into bodies of the dimensions desired for the growth of carbon fibrils.
29. Polymers into which clusters of carbon fibrils according to claims 20 through 24 have been processed.
30. Particles according to claims 1 through 9 and 19 through 24, on the surface of which catalytically active materials are provided.
31. Use of the particles according to claims 1 through 9 and 19 through 24 and 30, wherein the particles are suspended in a liquid phase and following the catalytic reaction are separated with an inhomogeneous magnetic field.

32. Use of particles according to claims 1 through 9 and 19 through 24 for the separation of proteins or biological cells.
33. Particles according to claims 1 through 9 and 19 through 24, the surface of which has been mildly oxidized and on which positively charged precursors of catalytically active materials are adsorbed from a solution.
34. Loading of particles according to claims 1 through 9 and 19 through 24 by providing extremely small metal particles on the surface and subsequently allowing these particles to grow either with the same material or with a different material through catalyzed reduction of dissolved compounds.
35. Particles according to claims 1 through 9 and 19 through 24 having on the surface a thin, amorphous layer of oxygen-containing carbon.
36. Loading of particles according to claims 1 through 9 and 19 through 24 with an amorphous layer of oxygen-containing carbon by impregnation with a glucose or sugar solution, drying and heating in an inert gas or an inert gas flow.
37. Reduction of noble metal precursors provided on supports according to claims 1 through 9 and 19 through 24 and 35 by heating in an inert gas or an inert gas flow.
38. Providing precursors of active components on the surface of the materials by priorly treating with surface-active compounds or impregnating with solutions of complexes of organic compounds, such as EDTA or citric acid, and subsequently heating in an inert gas, whereafter the carbon residues are removed and the active precursors, if necessary, are reduced under conditions where the hydrogen and methane partial pressure is set at such a value that the value of $p_{H_2}^2/p_{CH_4}$ lies between the value for the equilibrium between the metal carbide, hydrogen and methane and that between graphite, hydrogen and methane neither hydrogenation of carbon to methane nor formation of metal carbide arises.

39. Catalysts wherein on materials according to claims 1 through 9 and 19 through 24 cobalt and molybdenum or nickel and tungsten or mixtures of these components are provided.
40. Preparation of catalysts according to claims 36, 5 starting from molybdenum(III) chloride or tungsten(III) chloride which is oxidized in a suspension of the support to be loaded.
41. Ziegler-Natta or metallocene catalysts for the polymerization of olefins provided on clusters of carbon 10 fibrils according to claims 19 through 24.
42. Zeolites provided on carbon fibrils according to claims 19 through 24, whereafter the carbon, if necessary, is oxidized off.
43. Materials according to claims 1 through 9 and 19 15 through 24, wherein the carbon is wholly or partly converted to silicon carbide or through oxidation to silicon dioxide.
44. Ion exchangers by providing ion-exchanging groups on materials according to claims 1 through 9 and 19 through 24, 20 by, for instance, a mild oxidation or by reaction with sulfuric acid.
45. Ion exchangers by providing ion-exchanging components, such as sulfonated (poly)styrene or Nafion on materials according to claims 1 through 9 and 19 through 24.
46. Support bodies expanded with carbon fibrils, of 25 supports such as aluminum oxide, silicon dioxide, titanium dioxide, zirconium oxide or magnesium oxide.
47. Manufacture of support bodies expanded with carbon fibrils by loading with precursors of metals from which 30 metals and growth of carbon fibrils.
48. Electrodes at least partly consisting of particles according to claims 1 through 9 and 19 through 24, which are fixed through placement in a suitable magnetic field.
- Use of electrodes according to claim 48 for the production of 35 H_2O_2 .

Fig. 1

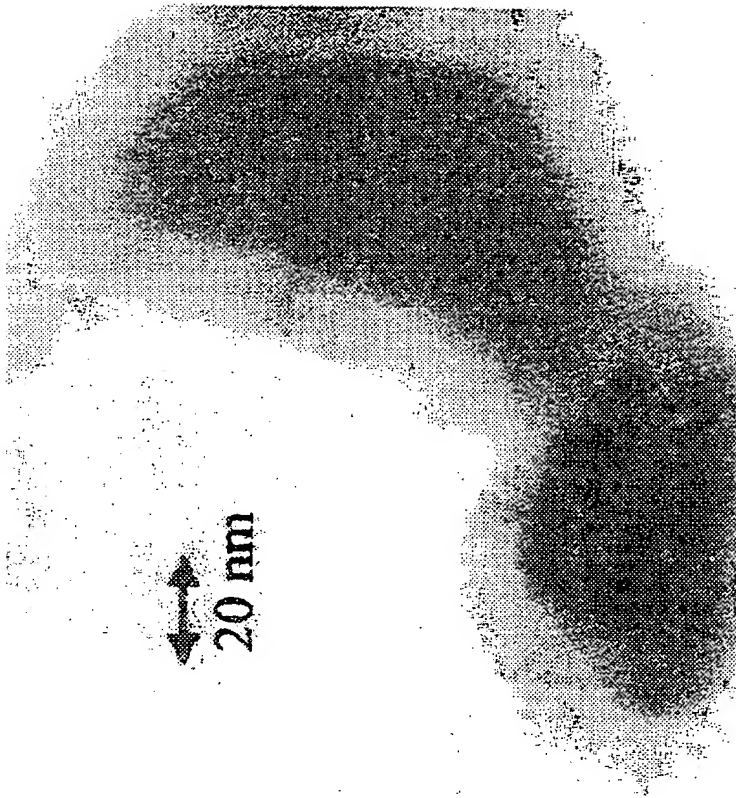


Fig. 2



SUBSTITUTE SHEET (RULE 26)

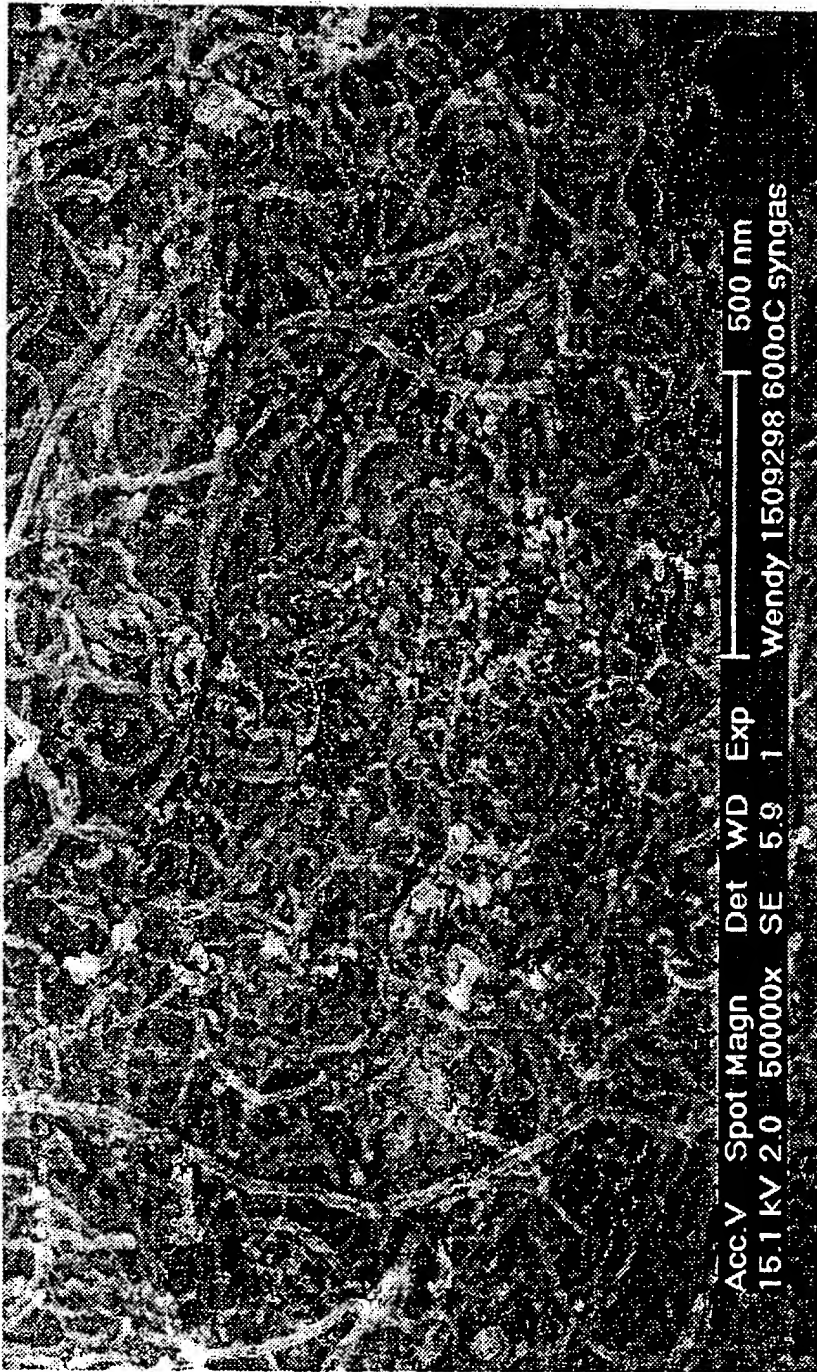


Fig. 3